

# Synthesis, crystal structures and photocatalytic properties of four silver(I) coordination polymers based on semirigid bis(pyrazole) and carboxylic acid co-ligands

Dian-Heng Huan<sup>1</sup> · Yan-Qin Zhao<sup>1</sup> · Gui-Ying Dong<sup>1</sup> · Fu-Jun Yin<sup>2</sup> · Sheng-Chun Wang<sup>1</sup>

Received: 10 April 2016/Accepted: 1 June 2016 © Springer International Publishing Switzerland 2016

Abstract Four Ag(I) coordination polymers, formulated as  $[Ag(L1)(tpa)_{0.5}]_n$  (1),  $\{[Ag(L2)(ndc)_{0.5}] \cdot 0.5H_2ndc\}_n$ (2),  $[Ag(L3)_{0.5}(ndc)_{0.5}]_n$  (3) and  $\{[Ag(L3)] \cdot H_3bptc\}_n$  (4) (L1 = 4,4'-bis(pyrazole-1-ylmethyl)-biphenyl, L2 = 4,4'bis(3,5-dimethylpyrazol-1-ylmethyl)-biphenyl, L3 = 1,4bis(3,5-dimethylpyrazol-1-ylmethyl)benzene,  $H_2$ tpa = terephthalic acid,  $H_2ndc = 2,6$ -naphthalenedicarboxylic acid.  $H_4$ bptc = 3,3',4,4'-biphenyltetracarboxylic acid). have been hydrothermally synthesized and structurally characterized. Complex 1 features the rare binodal (4,4)connected 2D 4,4L10 topological network with a point symbol of  $\{3^2 \cdot 4.6^2 \cdot 7\}_2 \{3^2 \cdot 6^2 \cdot 7^2\}$ . Complex **2** has a folded ladder-like chain structure, which is further extended into a 3D supramolecular network via O-H···O hydrogen bonding and  $\pi \cdots \pi$  stacking interactions. Complexes 3 and 4 both possess 1D zigzag chain structures. Complex 3 is further extended into a binodal (3.4)-connected network with the point symbol of  $\{4.8^4 \cdot 10\}\{6^2 \cdot 8^2\}_2$  by Ag...O weak interactions, while complex 4 is further connected through

**Electronic supplementary material** The online version of this article (doi:10.1007/s11243-016-0071-2) contains supplementary material, which is available to authorized users.

Gui-Ying Dong tsdgying@126.com

- Sheng-Chun Wang tswlhx@126.com
- <sup>1</sup> College of Chemical Engineering, Hebei Key Laboratory for Environment Photocatalytic and Electrocatalytic Materials, North China University of Science and Technology, Tangshan 063009, Hebei, People's Republic of China
- <sup>2</sup> Jiangsu Marine Resources Development Research Institute, Huaihai Institute of Technology, Lianyungang 222005, Jiangsu, People's Republic of China

O–H···O hydrogen bonding and  $\pi$ ··· $\pi$  interactions to afford a 2D supramolecular structure. The photoluminescence spectra and photocatalytic properties of these complexes for degradation of methylene blue and methyl orange are reported.

# Introduction

The crystal engineering of supramolecular architectures based on metal and mixed organic building blocks has attracted much attention, owing to their fascinating network topologies, as well as potential applications in various fields such as catalysis [1], luminescence [2], gas storage [3], molecular magnetism [4] and ion exchange [5]. In contrast to other transition metals, Ag(I) has a tendency to display highly versatile and irregular coordination numbers and geometries (linear, trigonal, tetrahedral, square planar and square pyramidal) because of its stable  $d^{10}$  closed-shell electronic configuration. This in turn results in a wide variety of sophisticated coordination architectures, including grids [6], helicates [7], cyclic helicates [8] and clusters [9]. In addition, Ag(I) coordination polymers (CPs) often show Ag. Ag [10], Ag.  $\pi$  [11], Ag. N [12] and Ag. O [13] interactions, as well as noncovalent intermolecular interactions such as hydrogen bonding [14] and  $\pi \cdots \pi$ interactions [15], as well as exhibiting high-dimensional structures and interesting optoelectronic properties. However, it is still difficult to control the final supramolecular architectures because of various parameters such as the selection of metals with different coordination geometries [16], the nature of the ligands used [17], the metal-ligand ratio [18], solvent system [19], pH of the reaction [20] and temperature [21].

The synthetic strategy of mixing both N-donor and polycarboxylate ligands has been proved to be a fruitful approach for the construction of CPs with intriguing multidimensional structures. Polycarboxylates such as terephthalic acid (H<sub>2</sub>tpa), 2,6-naphthalenedicarboxylic acid (H<sub>2</sub>ndc) and 3,3',4,4'-biphenyltetracarboxylic acid (H<sub>4</sub> bptc) are often used as multifunctional organic ligands, not only because of their various coordination modes, which is beneficial for the construction of CPs [22], but also because of their ability to act as hydrogen bond acceptors and donors in the assembly of supramolecular structures [23]. In recent years, bis(pyrazoles), as an important family of semirigid N-donor ligands, have attracted great interest [24, 25]. A rigid phenyl center linking two coordinating groups via flexible methylene (-CH2-) linkers confers on these ligands both flexibility and rigidity, leading to different conformations and coordination modes in a variety of supramolecular coordination complexes. Moreover, the pyrazole rings and larger conjugated  $\pi$  systems facilitate both hydrogen bonding and  $\pi \cdots \pi$  stacking interactions. For example, Shi's group has synthesized a variety of transition metal (Cu, Zn, Ag, Cd) CPs based on p-bis[(1-pyrazolyl)methyl] benzene ligands [26]. To the best of our knowledge, however, 4,4'-bis(pyrazole-1-ylmethyl)-biphenyl (L1), 4,4'-bis(3,5-dimethylpyrazol-1-ylmethyl)-biphenyl (L2) and 1,4-bis(3,5-dimethylpyrazol-1-ylmethyl) benzene (L3), as semirigid bis(pyrazolyl) ligands, have been little used to prepare Ag(I) CPs generated from mixed-ligand systems with interesting structures and functional properties, in particular photocatalytic properties. Therefore, in order to further study the structures and photocatalytic properties of ternary mixed Ag(I) CPs, we selected these compounds as N-donor co-ligands.

Herein, we report four silver(I) coordination polymers derived from semirigid bis(pyrazolyl) ligands: [Ag(L1) $(tpa)_{0.5}]_n$  (1), { $[Ag(L2)(ndc)_{0.5}] \cdot 0.5H_2ndc\}_n$  (2),  $[Ag(L3)_{0.5}$  $(ndc)_{0.5}]_n$  (3) and { $[Ag(L3)] \cdot H_3$ bptc}<sub>n</sub> (4). All four complexes were characterized by elemental analysis, IR spectroscopy, thermogravimetric analyses (TGA) and powder X-ray diffraction (PXRD). Furthermore, the photoluminescence and photocatalytic properties of these complexes are presented.

# **Experimental**

## Materials and measurements



Scheme 1 Three semirigid bis(pyrazole) ligands in this work

were recorded on a Perkin-Elmer automatic analyzer. IR spectra (KBr pellets) were obtained on a Nicolet IR Avatar 360 spectrophotometer in the range of 4000–400 cm<sup>-1</sup>. Thermogravimetric analyses experiments (TGA) were performed on a Netzsch TG 209 thermal analyzer under an N<sub>2</sub> atmosphere with a heating rate of 10 °C/min. Powder X-ray diffraction (PXRD) patterns were recorded with a D/MAX 2500PC diffractometer at 40 kV, 100 mA with Cu–K $\alpha$  radiation ( $\lambda = 1.5418$  Å). Solid-state fluorescence spectra were obtained with a Hitachi F-7000 fluorescence spectrophotometer at room temperature. The solid-state UV–Vis diffuse reflectance spectra were measured using a UV–Vis spectrophotometer, and a BaSO<sub>4</sub> plate was used as the reflectance standard.

# Synthesis of complex 1

A mixture of AgNO<sub>3</sub> (17.0 mg, 0.1 mmol), L1 (31.4 mg, 0.1 mmol), H<sub>2</sub>tpa (33.2 mg, 0.2 mmol) and distilled water (10 mL) was stirred for 30 min and then transferred to a 25-mL Teflon-lined container and kept under autogenous pressure at 120 °C for 3 days. After cooling to room temperature at a rate of 10 °C/h, colorless block single crystals of complex **1**,  $[Ag(L1)(tpa)_{0.5}]_n$ , were obtained with a yield of 61.4 % (based on Ag). Anal. Calcd. for C<sub>24</sub>H<sub>20</sub>AgN<sub>4</sub>O<sub>2</sub> (Fw = 504.31): C, 57.2; H, 4.0; N, 11.1 %. Found: C, 57.3; H, 4.0; N, 11.0 %. IR (KBr,

cm<sup>-1</sup>): 1599 s, 1518 m, 1400 s, 1281 m, 1093 m, 1055 m, 758 s, 744 m, 623 w.

# Synthesis of complex 2

The synthesis of complex **2** was analogous to that of complex **1**, except that L2 (37.0 mg, 0.1 mmol) and H<sub>2</sub>ndc (21.6 mg, 0.1 mmol) were used instead of L1 and H<sub>2</sub>tpa. Colorless block single crystals of complex **2**,  $\{[Ag(L2)(ndc)_{0.5}] \cdot 0.5H_2ndc\}_n$ , were acquired in 50.2 % yield based on AgNO<sub>3</sub>. Calcd. for C<sub>36</sub>H<sub>33</sub>AgN<sub>4</sub>O<sub>4</sub> (Fw = 693.53): C, 62.4; H, 4.8; N, 8.1 %. Found: C, 62.3; H, 4.7; N, 8.2 %. IR (KBr, cm<sup>-1</sup>): 1696 s, 1604 s, 1566 s, 1542 m, 1492 m, 1385 s, 1351 m, 1281 m, 1193 w, 1038 w, 782 s, 481 w.

# Synthesis of complex 3

The preparation of complex **3** was analogous to that of complex **2**, except that L2 was substituted by L3 (29.4 mg, 0.1 mmol). Colorless block single crystals of complex **3**,  $[Ag(L3)_{0.5}(ndc)_{0.5}]_n$ , were isolated in 56.2 % yield based on AgNO<sub>3</sub>. Calcd. for C<sub>15</sub>H<sub>14</sub>AgN<sub>2</sub>O<sub>2</sub> (Fw = 362.15): C, 49.7; H, 3.9; N, 7.7 %. Found: C, 49.7; H, 3.8; N, 7.8 %. IR (KBr, cm<sup>-1</sup>): 1615 s, 1568 s, 1401 s, 1341 s, 1290 m, 1183 m, 907 m, 776 s, 568 w, 479 w.

# Synthesis of complex 4

The preparation of complex **4** was analogous to that of complex **3**, except that H<sub>2</sub>ndc was substituted by H<sub>4</sub>bptc (33.0 mg, 0.1 mmol). Colorless block single crystals of complex **4**, {[Ag(L3)]·H<sub>3</sub>bptc}<sub>n</sub>, were obtained in 50.2 % yield based on AgNO<sub>3</sub>. Calcd. for C<sub>34</sub>H<sub>31</sub>AgN<sub>4</sub>O<sub>8</sub> (Fw = 731.50): C, 55.8; H, 4.2; N, 7.7 %. Found: C, 55.9; H, 4.1; N, 7.6 %. IR (KBr, cm<sup>-1</sup>): 1702 s, 1595 m, 1553 s, 1417 m, 1353 m, 1290 m, 1147 w, 874 w, 760 s, 644 m, 467 w.

# Photocatalytic experiments

The photocatalytic performance of each complex for the decomposition of MB or MO was measured by the following procedure: A 0.01 mol crystal sample of each title complex was mixed with 150 mL of MB or MO aqueous solution (20.0 mg  $L^{-1}$ ) and then magnetically stirred for about 30 min in the dark to obtain uniform working suspension. The suspension was then irradiated using a 500 W high-pressure mercury lamp, while continuously stirring with a magnetic stirrer. Aliquots (3 mL) of the suspension were taken out at given intervals, separated through centrifugation and then analyzed by UV–visible spectrophotometry. In

addition, control experiments for MB or MO degradation were performed under the same conditions without any catalyst. The characteristic peaks for methylene blue (664 nm) and methyl orange (506 nm) were used to monitor the photocatalytic decomposition process.

# X-ray crystallography

Crystallographic data for complexes 1–4 were collected on an Agilent SuperNova Dual diffractometer equipped with mirror monochromatic Mo– $K\alpha$  ( $\lambda = 0.71073$  Å) or Cu– $K\alpha$ ( $\lambda = 1.54184$  Å) radiation by using a  $\omega$  scan mode at 293(2) K, except for complex 2 which was analyzed at 100 K. CrysAlis<sup>PRO</sup> software was used to collect, index, scale and apply analytical absorption corrections based on faces of the crystal [29]. All of the structures were solved by direct methods and refined on  $F^2$  by full-matrix least squares methods using SHELXL-97 [30]. All non-hydrogen atoms were found from the Fourier difference maps and refined anisotropically. Crystallographic crystal data and structure processing parameters for the complexes are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

# **Results and discussion**

# Synthetic and spectral aspects

Silver(I) CPs generated from mixed-ligand systems can display a wide range of multidimensional structures and interesting properties [7–10]. In the present work, hydrothermal synthesis using different ligand combinations yielded new complexes, whose crystal structures were determined by X-ray diffraction analysis. The elemental analyses of the complexes **1–4** are in good agreement with the theoretical requirements of their compositions, and these complexes possess different polydimensional frameworks.

All four complexes are air-stable and insoluble in common solvents. In order to check their phase purities, their powder X-ray diffraction (PXRD) patterns were measured at room temperature (Fig. S1). The measured and simulated powder patterns are in good agreement, confirming the phase purities of the bulk materials.

In the IR spectra of complexes 1–4, the medium intensity bands from 1518 to 1568 cm<sup>-1</sup> are assigned to the v(C=N) stretching modes of the pyrazole rings. The  $v_{as}$  (COOH) bands of the uncoordinated carboxyl groups in complexes 2 and 4 were observed at 1696 and 1702 cm<sup>-1</sup>. The asymmetric and symmetric stretching vibrations of the carboxylate groups were observed at 1599 and 1400 cm<sup>-1</sup> for 1, 1604 and 1385 cm<sup>-1</sup> for 2, 1615 and 1401 cm<sup>-1</sup> for 3 and 1595 and 1417 cm<sup>-1</sup> for 4. The values of

Complex	1	2	3	4
Empirical formula	$C_{24}H_{20}AgN_4O_2$	C <sub>36</sub> H <sub>33</sub> AgN <sub>4</sub> O <sub>4</sub>	C <sub>15</sub> H <sub>14</sub> AgN <sub>2</sub> O <sub>2</sub>	C34H31AgN4O8
Formula weight	504.31	693.53	362.15	731.50
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	P2/c
Unit cell dimensions				
a/Å	8.4155(8)	10.6438(3)	7.5054(11)	13.6781(13)
b/Å	11.2864(8)	11.0943(4)	8.6213(12)	7.3157(7)
c/Å	11.9091(13)	14.2944(5)	12.0214(17)	15.9658(16)
α/°	82.8370(9)	110.907(3)	103.249(2)	90
β/°	81.7250(10)	92.143(3)	91.193(2)	96.3110(10)
γ <b>/</b> °	71.1400(10)	97.697(3)	110.792(2)	90
V/Å <sup>3</sup>	1055.56(17)	1555.99(9)	703.37(17)	1587.9(3)
Ζ	2	2	2	2
$Dc/g \text{ cm}^{-3}$	1.587	1.480	1.710	1.530
<i>F</i> (000)	510	712	362	748
Crystal size/mm	$0.22\times0.19\times0.19$	$0.25\times0.18\times0.17$	$0.29\times0.27\times0.25$	$0.23\times0.22\times0.20$
$\theta$ Range/°	2.47-27.57	3.32-76.03	2.61-27.56	2.57-27.55
Reflections collected	9811	17,711	6478	14,120
Independent reflections	4795	6315	3197	3643
R <sub>int</sub>	0.0218	0.0321	0.0245	0.0412
Absorption coefficient/mm <sup>-1</sup>	0.984	5.574	1.435	0.694
<i>T</i> /K	293(2)	100	293(2)	293(2)
Goodness of fit on F	1.020	1.106	1.011	1.041
Final <i>R</i> , wR <sub>2</sub> $[I > 2\sigma(I)]$	$R_1 = 0.0306$	$R_1 = 0.0337$	$R_1 = 0.0370$	$R_1 = 0.0414$
	$wR_2 = 0.0709$	$wR_2 = 0.0916$	$wR_2 = 0.0786$	$wR_2 = 0.1036$
R (all data)	$R_1 = 0.0370$	$R_1 = 0.0376$	$R_1 = 0.0565$	$R_1 = 0.0709$
	$wR_2 = 0.0749$	$wR_2 = 0.0942$	$wR_2 = 0.0878$	$wR_2 = 0.1168$
Largest diff. peak and hole	0.558, -0.699	0.593, -1.080	0.526, -0.374	0.661, -0.395

Table 1 Crystallographic data for complexes 1-4

 $\Delta v[v_{as}(COO)-v_s(COO)]$  indicate the presence of bridging (199 cm<sup>-1</sup> for **1**) and monodentate (219 cm<sup>-1</sup> for **2**, 214 cm<sup>-1</sup> for **3**) carboxylate groups [31].

#### Crystal structure of complex 1

Single-crystal X-ray diffraction analysis revealed that complex 1 crystallizes in the triclinic  $P_{\overline{1}}$  space group and exhibits a 2D coordination network. The asymmetric unit includes an independent Ag(I) center, one L1 ligand and half of a tpa ligand. As shown in Fig. 1a, each Ag center is surrounded by atoms O1A and O2 from two tpa ligands (Ag1–O1A 2.276(2), Ag1–O2 2.419(2) Å, symmetry code: A: -x, -y + 1, -z + 2), plus atoms N2B and N3 from two L1 ligands (Ag1–N2B 2.324(2), Ag1–N3 2.375(2) Å, symmetry code: B: -x, -y + 2, -z + 1) and the adjacent

Ag1 atom, forming a distorted square pyramidal geometry with a  $\tau_5$  value of 0.18 (for perfect square pyramidal geometry,  $\tau_5 = 0$ ). Remarkably, the Ag1–Ag1A distance of 2.8483(5) Å is comparable to the value of 2.89 Å in metallic silver and in the range expected for the sum of the covalent radii of two silver atoms (2.90 Å) [32], but significantly lower than twice the van der Waals radii of silver ions (3.44 Å) [33], indicating the existence of an argentophilic interaction. This argentophilic interaction is similar to those found in  $[Ag_6(p-mpspa)_6]^{6-}$  (2.8036(6) Å) (H<sub>2</sub>p-mpspa = 3-(4-methoxyphenyl)-2-sulfanylpropenoic acid) [10],  $[Sr_2Ag_4(HL)(H_2O)_{14}] \cdot 2H_2O$  (2.840 Å and 2.850 Å)  $(H_3L = 5$ -sulfo-salicylic acid) [34] and  $(Ag_2L_2)$ ·5AgCF<sub>3-</sub>  $CO_2 \cdot 5DMSO$  (2.742(8) Å) (H<sub>2</sub>L<sub>2</sub> = 9-(penta-1,4-diyn-3vlidene)-9H-fluorene) [35]. The bond angles around Ag(1) range from 71.05(4) to 126.33(7)°.

Parameter	Value	Parameter	Value
1			
Ag1–O1A	2.276(2)	Ag1–N2B	2.324(2)
Ag1–N3	2.375(2)	Ag1–O2	2.419(2)
Ag1–Ag1A	2.8483(5)		
O1A-Ag1-N3	103.68(7)	N2B-Ag1-N3	100.65(8)
O1A-Ag1-O2	137.06(7)	O1A-Ag1-N2B	92.19(7)
N3-Ag1-O2	84.14(7)	O1A-Ag1-N2B	126.33(7)
N2B-Ag1-Ag1A	100.28(6)	N3–Ag1–Ag1A	147.94(5)
O2-Ag1-Ag1A	71.05(4)	O1A-Ag1-Ag1A	82.74(5)
2			
Ag1–N4A	2.157(2)	Ag1–N1	2.162(2)
Ag1–O2	2.576(2)	N1-Ag1-O2	99.03(7)
N4A–Ag1–N1	162.86(9)	N4A-Ag1-O2	97.70(8)
3			
Ag1–N2	2.104(3)	Ag1–O2	2.113(2)
N2-Ag1-O2	174.85(10)		
4			
Ag1–N2A	2.099(3)	Ag1–N2	2.099(3)
N2A-Ag1-O2	175.94(14)		

Symmetry codes: for 1: A : -x, -y + 1, -z + 2; B: -x, -y + 2, -z + 1; for 2: A: x, y - 1, z; for 4: A: -x + 2, y, z + 3/2

In complex 1, each completely deprotonated  $\mu_4$ - $\eta^{1}, \eta^{1}, \eta^{1}, \eta^{1}, \eta^{1}$ -tpa ligand coordinates to four Ag(I) atoms through four carboxyl oxygen atoms, forming a 1D bimetallic [Ag<sub>2</sub>(tpa)]<sub>n</sub> chain (Fig. S2a). Simultaneously, two carboxylate groups clamp a pair of Ag(I) atoms to form ligand-supported argentophilic Ag...Ag interactions. Each trans-L1 ligand, in which the dihedral angle between the two parazole planes is  $82.89(13)^\circ$ , acts as  $\mu_2$ -bridging linker bridging two Ag atoms to form a dinuclear  $[Ag_2(L1)_2]$  secondary building unit (SBU) with a nonbonding Ag...Ag distance of 13.288 Å. Interestingly, adjacent [Ag<sub>2</sub>(L1)<sub>2</sub>] SBUs are linked by two closer Ag atoms with argentophilic Ag...Ag interactions to form infinite 1D loop-and-chain structures (Fig. S2b). The interlaced connection of the 1D chains of Ag(I)/tpa and Ag(I)/L1 units gives rise to a 2D framework showing a large window with dimensions of  $11.2864 \times 15.3522$  Å, involving shared Ag atoms (Fig. 1b). A better insight into the nature of this intricate framework was acquired by using TOPOS 4.0 software. The L1 ligands can be simplified as linear connectors; the Ag centers are considered as four-connected nodes, connected by two Ag atoms and two tpa ligands, while the tpa ligands linking four Ag atoms are viewed as four-connected nodes. This combination of nodes and connectors suggests a binodal (4,4)connected 4,4L10 network with a point symbol of  $\{3^2 \cdot 4.6^2 \cdot 7\}_2 \{3^2 \cdot 6^2 \cdot 7^2\}$  (Fig. 1c). To the best of our knowledge, although the present topological type has been theoretically predicted, this is the first example of a CP with the 4,4L10 topology.

#### Crystal structure of complex 2

X-ray crystallographic analysis revealed that complex 2 crystallizes in the triclinic crystal system and  $P_{\overline{1}}$  space group. The structure contains one crystallographically independent Ag(I) center, one L2 ligand, half of a completely deprotonated ndc ligand as well as half of a lattice ndc ligand in the asymmetric unit. The tricoordinate Ag1 atoms have a slightly distorted T-shaped geometry (Fig. 2a), provided by atom O2 of the  $\mu_2$ - $\eta^1$ , $\eta^1$ -ndc ligand (Ag1–O2 2.576(2) Å), plus atoms the N1 and N4A from two different  $\mu_2$ -L2 ligands with Ag1–N1 and Ag1–N4A distances of 2.162(2) and 2.157(2) Å, respectively. The values of the Ag–N and Ag–O bond lengths are in good agreement with those of similar Ag(I) complexes [36, 37].

In complex 2, for each of the *trans*-L2 ligands, the dihedral angle between parazole rings is  $8.76(10)^\circ$ . These bridge adjacent Ag atoms to form an infinite 1D  $[Ag(L2)]_n$ zigzag chain with a non-bonding Ag...Ag distance of 11.0943(5) Å (Fig. S3a). The completely deprotonated  $\mu_2$ - $\eta^{1}, \eta^{1}$ -ndc ligands link adjacent Ag atoms belonging to distinct  $[Ag(L2)]_n$  zigzag chains to form a folded ladderlike chain (Fig. S3b). The chains are further packed into a 2D supramolecular layer via O-H…O hydrogen bonding interactions between O3 and O1 from free and  $\mu_2$ - $\eta^1$ , $\eta^1$ ndc ligands (O3…O1 2.484(3)) (Fig. 2b). The adjacent 2D layers are further connected by two kinds of  $\pi \cdots \pi$  stacking interactions between parazole rings from distinct L2 ligands with centroid-to-centroid distances of 3.5865(19) and 3.6144(19) Å, respectively, resulting in a 3D supramolecular network (Fig. 2c).

#### Crystal structure of complex 3

Complex **3** crystallizes in the triclinic space group  $P\overline{1}$ . One Ag(I) center, half a L3 ligand and half a ndc ligand are located in the asymmetric unit. As shown in Fig. 3a, the central Ag1 is coordinated by atom N2 of the  $\mu_2$ -L3 ligand (Ag1–N2 2.104(3) Å) and atom O2 from the ndc ligand (Ag1–O2 2.113(2) Å) plus a weakly coordinated O2C atom from another ndc ligand (Ag1–O2C 2.733(3) Å, symmetry code: C: -x + 1, -y + 1, -z + 1). The N2–Ag1–O2 band angle is 174.84(10)°, consistent with a [2 + 1] T-shaped coordination geometry. The length of the Ag1–O2C bond 2.733(3) Å is significantly longer than normal, but shorter than the sum of the van der Waals radii of Ag and O (3.24 Å) and so can be regarded as a Ag…O interaction [38]. The Ag1–N2 and Ag1–O2 bond lengths fall in the expected ranges.

Fig. 1 a Coordination environment of Ag(I) center in complex 1 with 30 % thermal ellipsoids. Hydrogen atoms are omitted for clarity (symmetry code: A: -x, -y + 1, -z + 2; B: -x, -y + 2, -z + 1; C: -x, -y, -z + 2); b view of 2D framework of 1; c simplified view of the 2D binodal (4,4)connected 4,4L10 topology of 1



**(a)** 





Both the completely deprotonated ndc ligands and the *trans*-L3 ligand with two parallel parazole rings bridge adjacent Ag(I) atoms to give an infinite 1D [Ag<sub>2</sub> (L3)(ndc)]<sub>n</sub> zigzag chain (Fig. S4a), where the nonbonding Ag...Ag distances across the L and ndc ligands are

10.1264(12) and 13.2111(18) Å, respectively. As shown in Fig. 3b, adjacent 1D zigzag chains are extended to a 2D supramolecular network showing a large window with dimensions of  $16.6542(14) \times 19.1013(16)$  Å by means of Ag...O interactions. As for the topological geometry, the

Fig. 2 a Coordination environment of Ag(I) center in complex 2 with 30 % thermal ellipsoids. Hydrogen atoms are omitted for clarity (symmetry codes: A: x, y - 1, z; B: -x + 2, -y + 1, -z + 1); b view of the 2D supramolecular layer formed by strong O–H···O hydrogen bonding interactions in 2; c view of the 3D supramolecular framework formed by  $\pi \cdots \pi$ stacking and hydrogen bonding interactions of 2



(a)



**(b)** 





Ag centers and ndc ligands can be considered as fourconnected nodes and the L3 ligands can be simplified as linear connectors. The 2D framework can then be simplified as a new binodal 3,4-connected topology with the point symbol of  $\{4\cdot8^4\cdot10\}\{6^2\cdot8^2\}_2$  (Fig. 3c).

#### Crystal structure of complex 4

Complex **4** crystallizes in the monoclinic space group *P2/c*. One Ag(I) center, one L3 ligand and one lattice bptc ligand are located in the asymmetric unit. As shown in Fig. 4a, the

Ag1 center is linearly coordinated by atoms N2 and N2A from two neighboring L3 ligands (Ag1–N2 2.099(3) Å, Ag1–N2A 2.099(3) Å, symmetry code: A: -x + 2, -y + 1, -z + 1). The values of the Ag–N and Ag–O bond lengths are in good agreement with those observed in similar Ag(I) complexes.

Each L3 ligand adopts *trans*-conformation, with two parallel parazole rings bridging the adjacent Ag(I) atoms into an infinite 1D  $[Ag(L3)]_n$  zigzag chain, in which the nonbonding Ag...Ag distance across two distinct L3 ligands is 8.2160(8) (Fig. S5a). Each lattice bptc ligand

Fig. 3 a Coordination environment of Ag(I) center in complex 3 with 30 % thermal ellipsoids. Hydrogen atoms are omitted for clarity; b view of 2D supramolecular network of 3 formed by Ag…O interactions; c simplified view of the 2D binodal 3,4-connected new topology of 3





Fig. 4 a Coordination environment of Ag(I) center in complex 4 with 30 % thermal ellipsoids. Hydrogen atoms are omitted for clarity; **b** view of 2D supramolecular layer formed by  $\pi \cdots \pi$  stacking interactions and hydrogen bonding interactions of 4



connects another two into a 1D linear chain by O–H…O hydrogen bonding interactions between O1 and O1B from different bptc ligands (O1…O1B 2.449 (3) Å) (Fig. S5b). The two kinds of chains are further connected through  $\pi$ … $\pi$  interactions between the parazole rings of L3 and benzene rings of ndc ligands with a centroid-to-centroid distance of 3.6511(19) Å, yielding a 2D supramolecular layer (Fig. 4b).

#### **Thermal properties**



To investigate the thermal stabilities of the complexes, thermogravimetric analysis (TGA) was performed at room

Fig. 5 TGA curves of complexes 1-4

temperature to 800 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. As shown in Fig. 5, the TGA analysis revealed that these complexes were quite stable up to 200 °C. Complex 1 revealed a two-step weight loss process. The first step occurred from 226 to 325 °C with a weight loss of 61.5 %, which can be ascribed to the loss of L1 ligand (calcd: 62.3 %). The second step was observed in the range from 371 to 503 °C, corresponding to the release of tpa ligand and resulting in the complete decomposition of the complex with 23.7 % residual weight corresponding to Ag<sub>2</sub>O (calcd: 23.0 %). In complexes 2-4, only one weight loss of 82.4 % from 204 to 640 °C (calcd: 83.3 %) for 2, 67.6 % from 216 to 645 °C (calcd: 68.0 %) for 3 and 84.7 % from 210 to 519 °C (calcd: 84.2 %) for 4 was observed, accompanying the loss of total organic ligands. The final residues of all the title complexes correspond to  $Ag_2O$ .

# **Photoluminescence** properties

Hybrid CPs, especially those with  $d^{10}$  metal centers, have been widely found to present photoluminescence properties and may find applications as photoluminescent materials [39]. The photoluminescence properties of the Ag(I) complexes 1–4 as well as the corresponding free ligands (L1, L2 and L3) in the solid state have been investigated at room temperature (Fig. 6). The free ligands L1, L2 and L3 show intense emission bands with maxima at 330, 421 and 288 nm upon excitation at 245, 350 and 250 nm, respectively, which may be attributed to  $\pi^* \rightarrow \pi$  or  $\pi^* \rightarrow n$ 



Fig. 6 Solid-state photoluminescence spectra of complexes 1-4 as well as the corresponding ligands (L1, L2 and L3)

transitions [40]. The emission peaks of the complexes occur at 372 nm ( $\lambda_{ex} = 300 \text{ nm}$ ) for **1**, 489 nm ( $\lambda_{ex} = 250 \text{ nm}$ ) for **2**, 400 nm ( $\lambda_{ex} = 300 \text{ nm}$ ) for **3** and 380 nm ( $\lambda_{ex} = 275 \text{ nm}$ ) for **4**, which are red-shifted by 42 nm (**1**), 68 nm (**2**), 112 nm (**3**) and 92 nm (**4**) compared with the corresponding free ligands. These emissions may be assigned to ligand-to-metal charge transfer (LMCT) transitions [41].

# Optical and photocatalytic properties

The UV–Vis spectra of the complexes were recorded in the crystalline state at room temperature. As depicted in Fig. S6, all spectra show absorption components ascribed to  $\pi \rightarrow \pi^*$  transitions of the ligands, while the main UV absorption bands at 285, 280, 277 and 292 nm for complexes 1–4, respectively, can be attributed to LMCT transitions [42]. In order to investigate the semiconductor properties of the complexes, their diffuse reflectance data were transformed using the Kubelka–Munk function to obtain their band gaps ( $E_g$ ). As shown in Fig. 7, the  $E_g$  values evaluated from the steep absorption edge are 3.23 eV for 1, 3.24 eV for 2, 3.31 eV for 3 and 3.35 eV for 4. These band gap values suggest that complexes 1–4 may be responsive to UV light and so have potential to mediate photocatalytic reactions.

Photocatalytic degeneration of organic pollutants has become one of the most green and efficient technologies for environmental remediation, and much effort has been devoted to studying CPs as photocatalysts for the degradation of organic dyes. Methyl orange (MO) and methylene blue (MB) provide two examples of poorly biodegradable dyes, as found in wastewater of the textile industry [43]. Therefore, we selected MO and MB as model pollutants in order to evaluate the photocatalytic activities of complexes



Fig. 7 Diffuse reflectance spectra of Kubelka–Munk function versus energy of complexes 1-4

![](_page_9_Figure_10.jpeg)

Fig. 8 Absorption spectra of the MB (a) and MO (b) solution during decomposition reaction under UV irradiation in the presence of complex 1

1–4. As shown in Figs. 8, S7 and S8, little change in the degradation of MB or MO was observed in the control experiments. In contrast, the absorption intensities of MB or MO reduced gradually with increasing irradiation times when using each of these complexes as a photocatalyst. As shown in Fig. 9a, the degradation efficiency of MB [9] increased from 11.1 % (without any catalyst) to 92.8 % for complex 1, 59.7 % for complex 2, 72.6 % for complex 3 and 72.5 % for complex 4 after 120 min of irradiation. Similarly, in Fig. 9b, the degradation efficiency of MO increased from 10.1 % (without any catalyst) to 84.8 % for complex 1, 56.7 % for complex 2, 77.6 % for complex 3 and 68.6 % for complex 4 after 120 min of irradiation. It is evident that the photodegradation performances of complex 4 for both MB and MO under UV light are better than those of complexes 1-3. An additional control experiment using an equimolar amount of AgNO<sub>3</sub> under the same conditions showed no observable photocatalytic activity.

![](_page_10_Figure_2.jpeg)

Fig. 9 Decomposition of MB (a) and MO (b) solution in a photocatalytic process

It is noteworthy that the photocatalytic efficiencies of the present complexes were higher than those obtained with other CPs under UV irradiation as reported recently. For example, Ma's group has reported three complexes, which exhibited photodegradation activities for MB under UV light, with degradation ratios for MB after 150 min of 39, 27 and 58 %, which are lower values than those of complexes 1-4 [44]. Moreover, the photocatalytic activities of the present complexes toward MO are higher than those of complexes reported by Wang's group, where the degradation ratios for MO were 27.8, 29.6, 75.8 and 76.6 % [45]. Returning to the present complexes, their PXRD patterns were measured after the catalytic experiments and found to be nearly identical to those of the original complexes (Fig. S1), implying good stability in the photocatalytic degradation experiments.

Although the value of the band gap  $E_g$  is an effective indicator of the photocatalytic properties, the structures of the complexes are also important [46–48]. Thus, complex **1** is expected to be the most active of the complexes, since it has the smallest band gap. Besides, the 2D structure of complex **1** shows a large open channel with dimensions of 15.7945(8) × 12.1963(8) Å, which should be conducive to the transport of excited holes/electrons to its surface. Although the band gap of complex **2** is not the largest, it has the lowest degradation rates for MB and MO, which may result from its dense 3D supramolecular structure. Because our photocatalytic reaction is heterogeneous, we speculate that multihole catalysts with more extended networks may be beneficial to improve catalyst activity.

# Conclusion

In this work, we have assembled four Ag(I) CPs from carboxylic acid and semirigid bis(pyrazole) ligands under hydrothermal conditions. The polycarboxylate ligands, exhibiting rich coordination modes, have great influence on the structural diversities of these complexes, while the semirigid bis(pyrazole) ligands with different conformations and coordination modes help to shape the network structures of these complexes. Under UV irradiation, these complexes exhibited high catalytic activities for the photodegradation of MB and MO, implying that they may be potential catalysts for the photodecomposition of organic pollutants in industrial wastewater.

## **Supplementary materials**

CCDC 1427868, 1465080, 1465081 and 1465082 contain the supplementary crystallographic data for complexes 1–4. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/deposit or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments The project was supported by the National Natural Science Foundation of China (51474086), Natural Science Foundation—Steel and Iron Foundation of Hebei Province (B2015209299).

### References

- Cui GH, He CH, Jiao CH, Geng JC, Blatov VA (2012) CrystEngComm 14:4210–4216
- Shustova NB, McCarthy BD, Dinca M (2011) J Am Chem Soc 133:20126–20129
- Rosi NL, Eckert J, Eddaoudi M, Vodak DT, Kim J, O'Keeffe M, Yaghi OM (2003) Science 300:1127–1129
- 4. Li HH, Shi W, Xu N, Zhang ZJ, Niu Z, Han T, Cheng P (2012) Cryst Growth Des 12:2602–2612
- 5. Wang JC, Liu QK, Ma JP, Huang F, Dong YB (2014) Inorg Chem 53:10791–10793
- Jaros SWM, Guedes da Silva MFC, Florek M, Oliveira MC, Smolenski P, Pombeiro AJ, Kirillov AM (2014) Cryst Growth Des 14:5408–5417
- 7. Stephenson A, Ward MD (2012) RSC Adv 2:10844-10853
- Argent SP, Adams H, Riis-Johannessen T, Jeffery JC, Harding LP, Mamula O, Ward MD (2006) Inorg Chem 45:3905–3919
- 9. Hao JM, Yu B, Hecke KV, Cui GH (2015) CrystEngComm 17:2279–2293
- Barreiro E, Casas JS, Couce MD, Laguna A, López-de-Luzuriaga JM, Monge M, López EMV (2013) Dalton Trans 42:5916–5923
- Liang MX, Ruan CZ, Sun D, Kong XJ, Ren YP, Long LS, Zheng LS (2014) Inorg Chem 53:897–902
- 12. Huan DH, Liu YG, Yu B, Hecke KV, Cui GH (2016) Inorg Chem Commun 67:17–21
- Sun D, Wei ZH, Wang DF, Zhang N, Huang RB, Zheng LS (2011) Cryst Growth Des 11:1427–1430
- Wang XX, Liu YG, Ge M, Cui GH (2015) Chinese. J Inorg Chem 31:2065–2072
- 15. Salonen LM, Ellermann M, Diederich F (2011) Angew Chem 123:4908–4944
- 16. Liu GZ, Wang JG, Wang LY (2012) CrystEngComm 14:951-960
- 17. Wang XX, Yu B, Hecke KV, Cui GH (2014) RSC Adv 4:61281–61289
- Zhao XL, Zhang LL, Ma HQ, Sun D, Wang DX, Feng SY, Sun DF (2012) RSC Adv 2:5543–5549
- 19. Li CP, Yu Q, Chen J, Du M (2010) Cryst Growth Des 10:2650–2660

- Su Z, Fan J, Okamura TA, Sun WY, Ueyama N (2010) Cryst Growth Des 10:3515–3521
- Zheng B, Dong H, Bai JF, Li YZ, Li SH, Scheer M (2008) J Am Chem Soc 130:7778–7779
- 22. Hu JM, Blatov VA, Yu B, Hecke KV, Cui GH (2016) Dalton Trans 45:2426–2429
- Dias SSP, André V, Kłak J, Duarte MT, Kirillov AM (2014) Cryst Growth Des 14:3398–3407
- 24. Christer BA, John D, Meg EF (2006) CrystEngComm 8:586-588
- 25. Hazel F, Ian ST, Michael DW (2011) CrystEngComm 13:1432–1440
- Wang XY, Liu SQ, Wei XL, Zhang CY, Song G, Bai FY, Xing YH, Shi Z (2012) Polyhedron 47:151–164
- 27. Hoskins BF, Robson R, Slizys DA (1997) J Am Chem Soc 119:2952–2953
- 28. Hartshorn CM, Steel PJ (1995) Aust J Chem 48:1587-1599
- 29. Agilent Technologies (2012) CrysAlis PRO Agilent Technologies, Yarnton, England
- Sheldrick GM (2008) Acta Crystallogr Sect A: Found Crystallogr 64:112–122
- 31. Deacon GB, Phillips RJ (1980) Coord Chem Rev 33:227-250
- Cordero B, Gómez V, Platero-Prats AE, Revés M, Echeverría J, Cremades E, Alvarez S (2008) Dalton Trans 21:2832–2838
- Bisht KK, Kathalikkattil AC, Suresh E (2012) RSC Adv 2:8421–8428
- 34. Li Q, Fu ML, Liu X, Guo GC, Huang JS (2006) Inorg Chem Commun 9:767–771
- 35. Hau SC, Mak TC (2013) Polyhedron 64:63-72
- Marcinkowski D, Wałęsa-Chorab M, Patroniak V, Kubicki M, Kądziołka G, Michalkiewicz B (2014) New J Chem 38:604–610
- 37. Kole GK, Chin CK, Tan GK, Vittal JJ (2013) Polyhedron 52:1440–1448
- 38. Yang L, Powell DR, Houser RP (2007) Dalton Trans 9:955-964
- 39. Sun D, Liu FJ, Huang RB, Zheng LS (2013) CrystEngComm 15:1185–1193
- 40. Xu JX, Wang RY, Li YM, Gao ZY, Yao R, Wang S, Wu BL (2012) Eur J Inorg Chem 20:3349–3360
- Sarma D, Ramanujachary KV, Lofland SE, Magdaleno T, Natarajan S (2009) Inorg Chem 48:11660–11676
- 42. Gong Y, Jiang PG, Wang YX, Wu T, Lin JH (2013) Dalton Trans 42:7196–7203
- Wang SL, Hu FL, Zhou JY, Zhou Y, Huang Q, Lang JP (2015) Cryst Growth Des 15:4087–4097
- 44. Zhang HM, Yang J, Kan WQ, Liu YY, Ma JF (2015) Cryst Growth Des 16:265–276
- 45. Wang XL, Gong CH, Zhang JW, Hou LL, Luan J, Liu GC (2014) CrystEngComm 16:7745–7752
- 46. Hu Y, Luo F, Dong FF (2011) Chem Commun 47:761-763
- Kan WQ, Liu B, Yang J, Liu YY, Ma JF (2012) Cryst Growth Des 12:2288–2298
- Liu L, Ding J, Li M, Lv XF, Wu J, Hou HW, Fan YT (2014) Dalton Trans 43:12790–12799